

III.B.1 Technology Development in Support of SECA

Objectives

- Improve the sulfur tolerance of diesel reforming catalysts.
- Determine long-term stability.
- Determine effects of polyaromatics on catalyst activity.

Approach

- Synthesize and characterize perovskites that are stable in hydrogen and oxygen and have redox chemistry on the “B” site.
- Verify that the doped catalysts are chemically and thermally stable and relatively unaffected by sulfur containing fuel.
- Determine reforming efficiency of fuels with sulfur and polyaromatics.

Accomplishments

- The new perovskite catalysts were shown to maintain their activity over 1000 hours in reducing and oxidizing environments.
- Polyaromatics were shown to deactivate the catalyst to some extent and may require alternative treatment.

Future Directions

- Explore materials or engineering improvements to deal with polyaromatics.
- Assist vertical teams to address reformer engineering issues.

Michael Krumpelt (Primary Contact), Di-Jia Liu
Argonne National Laboratory
Argonne, IL 60439
Phone: (630) 252-8520; Fax: (630) 252-4176
E-mail: krumpelt@cmt.anl.gov

DOE Project Manager:
Ayyakkannu Manivannan
Phone: (304) 285-2078
E-mail: Ayyakkannu.Manivannan@netl.doe.gov

Introduction

Auxiliary power units (APUs) for heavy-duty vehicles could reduce emissions and conserve fuel on the North American continent, where engines are kept running while drivers rest. An APU must have enough power to keep the cabin cooled or heated in hot or cold climatic conditions, respectively, and may have to also supply electricity for refrigeration of cargo. The amount of fuel needed will be significant and drivers may resist having to refuel the APU with anything other than the diesel fuel used for the engine.

Converting diesel fuel into a hydrogen-rich gas that is suitable for solid oxide fuel cells is more challenging than converting gasoline because of the multi-cyclic aromatics and the aromatic sulfur compounds in diesel fuel. The sulfur in the fuel adsorbs or reacts with the metal catalyst, deactivating it. Similarly, the poly-aromatics adsorb on the catalyst, and because the kinetics of breaking the H-C and C-C bonds in polyaromatics are slower than in paraffins and olefins, the catalyst becomes less active. Also, the unreacted aromatics tend to form coke. To mitigate these issues, the operating temperature of the reformer must be raised, but this causes the presently used nickel or rhodium catalysts to agglomerate and evaporate.

Approach

At Argonne, we have been actively exploring alternative catalysts that could reduce the material cost yet maintain or improve catalytic activity. In the last two years, we actively engaged the investigation of perovskites as diesel reforming catalyst material due to their propensity to form oxide ion vacancies and electron conductivity. Perovskite is a combination of metal oxides with a typical formulation of ABO_3 , where A and B are the elements from alkaline, alkaline earth, and transitional metal groups. The A site ion occupies a dodecahedral interstice coordinated with 12 O, which in turn belongs to eight BO_6 octahedra sharing the corners. The stability is attributed primarily to the Madelung energy of the stacking of rigid BO_6 . Both A and B sites in perovskite can be partially exchanged to form $A_{1-x}A'_x B_{1-y}B'_y O_3$, resulting in mixed valance states and enhanced mobility of oxygen in the lattice. In our study, we found that the exchange of the B site can often lead to significant improvement in catalytic reforming activity. For example, we have successfully exchanged

ruthenium in LaCrO_3 and found the catalyst provides excellent hydrogen yield, reforming efficiency, and sulfur tolerance during the autothermal reforming study. To further prove that perovskite can be indeed used as the practical catalyst for commercial applications, a series of experiments need to be carried out to test the performance with real commercial diesel and at extended operating duration.

Results

Commercial diesel fuel is a complicated mixture of a variety of hydrocarbons and sulfur containing compounds. The key composition of diesel fuel includes paraffins, naphthenes, and mono- and multiple ring aromatics. The catalytic chemistry of each component could be significantly different. More importantly, the cross-interference between different components can significantly complicate the overall reforming chemistry and efficiency. We conducted a systematic study to address the influence on reforming performance from each main group represented by the fuel blend of dodecane (DDN), butylcyclohexane, decalin, butylbenzene, tetralin and 1-methylnaphthylene (1MN). We found that the reforming efficiency and COx selectivity under identical reaction conditions follow the order of paraffins \approx cycloparaffins $>$ mono-aromatics \gg poly-aromatics whereas the formation of residual hydrocarbons mainly in the form of fragmented C2, C3, etc., follows the reversed order. We interpret this trend as the result of rate difference in hydrocarbon decomposition. Aromatics, especially heavy aromatics, have extended π -orbital conjugation and C=C bond is more difficult to be cleaved than alkanes and olefins.

To understand the synergetic effect from different fuel components, we also formulated a simulated diesel containing all aforementioned hydrocarbons, in addition to a representative organic sulfur compound, dibenzothiophene (DBT) with an equivalent sulfur content of 50 ppm by weight. The simulated diesel has a composite molecular formula of $\text{C}_{10.7}\text{H}_{20.4}$ and heat of combustion is 6453 kJ/mole. For comparison, we also acquired a low-sulfur distillate, JP8, from a commercial source which contains about 60 ppm S by weight. The catalytic reforming study was carried out at 800°C with an oxygen-to-carbon ratio of $\text{O}_2/\text{C} = 0.5$ and steam-to-carbon ratio of $\text{H}_2\text{O}/\text{C} = 1$. The ATR reaction was performed at a gaseous hourly space velocity of 100,000 hr^{-1} for the better differentiation on the reaction kinetics. Figure 1 shows the total reforming efficiency and the selectivity towards COx for different fuel surrogates, simulated diesel and commercial JP8. We found that, with 5% 1MN in a dodecane mixture, the reforming efficiency is clearly affected by the cross-interference from the polyaromatic compound. The simulated diesel,

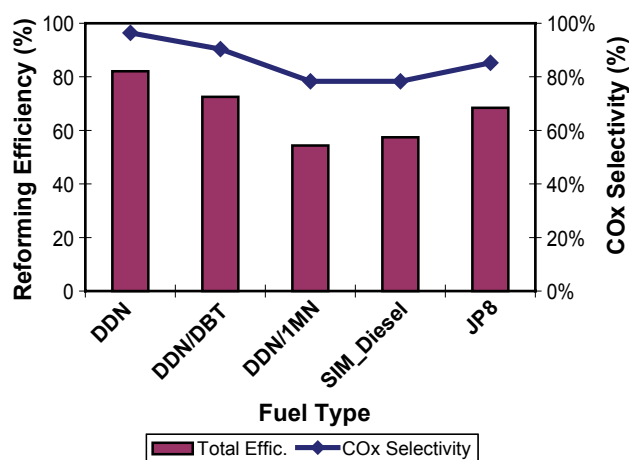


FIGURE 1. Reforming Efficiency and COx Selectivity of $\text{LaCr}_{0.95}\text{Ru}_{0.05}\text{O}_3$ Tested with Different Surrogate Diesel Fuels and JP8

with 3% 1MN but added with 7% monoaromatics, has reached somewhat better efficiency possibly due to the sensitivity towards polyaromatics. A very encouraging observation is that our catalyst performed respectably for the commercial JP8 with reforming efficiency in the 70% range and COx selectivity of near 90%, considered that the study was conducted at the kinetic differential region with low steam content. The performance will obviously improve significantly in an actual catalytic reactor which operates with slower space velocity.

Significant progress was also made to complete the 1000-hour aging study for our benchmark perovskite catalyst. Under ATR reactions, the catalyst is subject to interaction with both a strong reductant such as fuel, and oxidant such as air in the reformate stream. One of the major concerns is the stability of the active center during the repeated swing between reducing and oxidizing environments which could lead to bleaching of atomically dispersed ions such as Ru out of the perovskite lattice. To experimentally address this issue, we conducted two parallel durability tests where $\text{LaCr}_{0.95}\text{Ru}_{0.05}\text{O}_3$ catalyst was subjected to the treatments under either humidified air or simulated reformate containing H_2 , CO, CO_2 , CH_4 , N_2 and 26% H_2O . The aging was carried out at 800°C and a fraction of the sample was taken out in every 200 hours to be tested with various simulated fuel and JP8 at near differential flow conditions. Shown in Figure 2 are the total reforming efficiencies with each fuel at different stages of aging. The general observation suggests that slight degradation occurs although the rate depends on the type of the fuel tested. The reforming efficiency for our chromite catalyst held to about 10% deactivation at the end of test cycle.

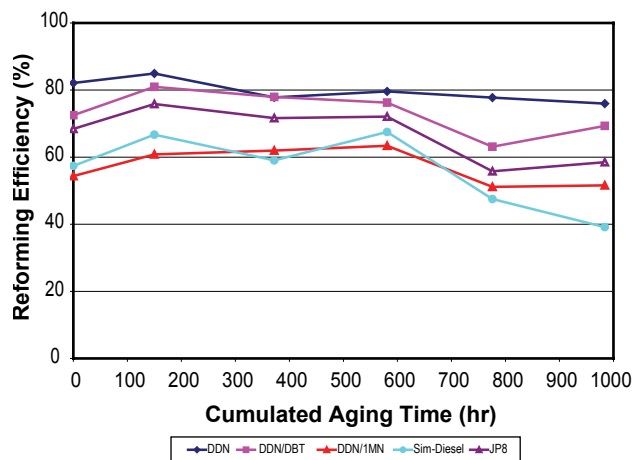


FIGURE 2. Reforming Efficiency of $\text{LaCr}_{0.95}\text{Ru}_{0.05}\text{O}_3$ for Surrogate Diesel Fuels and JP8 Tested at Various Stages of Aging during the 1000-Hour Durability Test in the Simulated Reformate Stream

FY 2006 Publication & Presentation

1. Activity and Structure of Perovskites as Diesel Reforming Catalysts for Solid Oxide Fuel Cell, D. J. Liu and M. Krumpelt, *International Journal of Applied Ceramic Technology*, Vol. **2**, No 4, Page 301-307, (2005).
2. Activity and Structure of Perovskites as Diesel Reforming Catalysts for Solid Oxide Fuel Cell, Di-Jia Liu and Michael Krumpelt, *Ceramic Engineering and Science Proceedings (CESP)*, Vol. **26**, No. 4, *Advances in Solid Oxide Fuel Cells*.
3. Critical Issues in Catalytic Diesel Reforming for Solid Oxide Fuel Cells, Di-Jia Liu, Mike Krumpelt, Hual-Te Chien and Shuh-Haw Sheen, to be published at *Journal of Material Engineering and Performance*.

Conclusion

- The reforming chemistry of the main hydrocarbon representatives in diesel was investigated. The cross-interference from the heavy polyaromatics to the overall reforming efficiency was identified.
- ATR reforming on commercial JP8 was studied and relatively good performance was observed with Argonne's perovskite catalyst.
- Two 1000-hour aging studies in both oxidative and reductive gas flow were carried out and our catalyst showed relatively good durability.